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The Solution and Solid State Analysis of Xylylic Di-copper Complexes as Receptors for Encapsulating Anions

James Rawiri Stevens

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Abstract

The investigation into neutral aryl-linked oxime dicopper helicates encapsulating a number of anions was carried out. Two dicopper aryl-linked salicyloxime derived complexes were synthesized and studied which contained either *p*-xylylic (1) or *m*-xylylic (2) incorporated spacer groups. UV-visible spectroscopy was used to determine the binding stability constants of the anion complexes. Complex binding, encapsulation of anions and the conformational flexibility of 1 and 2 was supported and ascertained by the crystal structural data obtained. Receptor 1 expressed an exceptional binding strength for sulfate in THF where a log $K$ value of $5.5 \pm 0.3$ was acquired. Receptor 2 could form both helical and non-helical structures. This was able to bind bromide selectively in a 2:1 stoichiometry of anion:receptor with a log $K_2$ value of $9.2 \pm 0.1$ and showed an unexpectedly high association constant for the perchlorate anion in a 1:1 stoichiometry with a log $K$ value of $4.6 \pm 0.2$ (presumably in a helical structure).
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Abbreviations

⊂ Indicates encapsulation of a guest molecule within a host molecule/complex.

1 Anion-free complex formed between Cu(II) acetate and ligand L₁. It is used within this report to represent the unprotonated complex [Cu₂(L¹-2H)₂].

1a N, N’-dimethyl-p-xylylenediamine.

1b 3, 3’-(1, 4-phenylenebis(methylene))bis(methylazanediyl)bis(methylene)bis(5-tert-butyl-2-hydroxybenzaldehyde).

2 Anion-free complex formed between Cu(II) acetate and ligand L², representing the unprotonated form [Cu₂(L²-2H)₂].

2a N, N’-dimethyl-m-xylylenediamine.

2b 3, 3’-(1, 3-phenylenebis(methylene))bis(methylazanediyl)bis(methylene)bis(5-tert-butyl-2-hydroxybenzaldehyde).

3 [ClO₄⊂(Cu₂L₁)₂](ClO₄)₃; the zwitterionic form with a captured perchlorate anion.

4 [BF₄⊂(Cu₂L₁)₂](BF₄)₃; the zwitterionic form with a captured tetrafluoroborate anion.

5 [NO₃⊂(Cu₂L₂)₂](NO₃)₃; the zwitterionic form with a captured nitrate anion.

6 [2Br⊂(Cu₂L₂)₂](Br)₂; the zwitterionic form with two captured bromide anions and two counter bromide anions.

7 [2Br⊂(Cu₂L₂)₂](BF₄)₂; the zwitterionic form with two captured bromide anions and two counter tetrafluoroborate anions.

CCDC Cambridge Crystallographic Data Centre.

CHCl₃ Chloroform.

DCE 1,2-dichloroethane.

DMSO-d₆ Deuterated dimethyl sulfoxide.
ESMS  Electro spray Ionization Mass Spectrometry.
IPA  Isopropanol.
IR  Infrared spectroscopy.
K  Formation constant. The equilibrium constant for the formation of a complex in solution. Also referred to as the binding, stability or association constant throughout the text.
L₁  \( (1E, 1'\E)\)-5-tert-butyl-3-(((4-(((5-tert-butyl-2-hydroxy-3-((E)-(hydroxyimino)methyl)benzyl)(methyl)amino)methyl)benzyl) (methyl)amino)methyl)-2-hydroxybenzaldehyde oxime.
L₂  \( (1E, 1'\E)\)-5-tert-butyl-3-(((3-(((5-tert-butyl-2-hydroxy-3-((E)-(hydroxyimino)methyl)benzyl)(methyl)amino)methyl)benzyl) (methyl)amino)methyl)-2-hydroxybenzaldehyde oxime.
MeOH  Methanol.
MeCN  Acetonitrile.
NMR  Nuclear magnetic resonance.
THF  Tetrahydrofuran.
TBABr  Tetra-\( n \)-butylammonium bromide.
t-Bu  tertiary butyl group or 1,1-dimethylethyl group ((CH₃)₂C−).
UV-vis  Ultraviolet-visible spectroscopy.